

**APPLICATION FOR UNITED STATES LETTERS PATENT**

TITLE: MANUFACTURING METHOD FOR MULTILAYER  
FLUORESCENT INFORMATION CARRIERS

APPLICANTS: GALINA DOROZHKINA  
IRINA KIRYUSHEVA  
EUGENE LEVICH  
ALEXEY LEZHNEV  
DMITRY PEBALK

ASSIGNEE: TRID STORE IP LLC  
SUITE 453, 230 PARK AVENUE  
NEW YORK, NEW YORK 10169

BLANK ROME COMISKY & McCAULEY LLP  
Wigman, Cohen, Leitner & Myers IP Group  
900 17th Street, N.W., Suite 1000  
Washington, D.C. 20006  
(202) 530-7400  
(202) 463-6915 (facsimile)

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# MANUFACTURING METHOD FOR MULTILAYER FLUORESCENT INFORMATION CARRIERS

## Reference to Related Application

This application claims the benefit of U.S. Provisional Application No. 60/176,294,  
5 filed January 18, 2000, whose disclosure is hereby incorporated by reference in its entirety  
into the present disclosure.

## Field of the Invention

The present invention is directed to a method of manufacturing a multilayer  
fluorescent information carrier and more particularly to such a method in which materials are  
10 applied under the action of centrifugal forces.

## Description of Related Art

In digital storage, whether of software, music, motion pictures, or the like, it has long  
been desired to store ever more information in ever less space. Compact discs have been in  
use for roughly two decades to store music, software, and other materials in digital form.  
15 However, the fact that a compact disc has only one recording layer limits its information  
capacity.

To increase the capacity relative to a traditional compact disc, optical memory media  
with multiple layers have been developed. However, when such media are read by reflection  
of coherent light, parasitic reflection can occur at layer boundaries. That reflection and the  
20 resulting interference impair reading.

One such device is the multilayer fluorescent information carrier, examples of which  
are disclosed in U.S. Patent No. 6,039,898, issued March 21, 2000, and in WO 99/47327 A1,  
published September 23, 1999. Such carriers exhibit high recording density, contrast, and  
signal-to-noise ratio. It is common to use fluorescent recording materials that, when exposed  
25 to reading light at one wavelength, fluoresce at a different wavelength. The problem of

parasitic reflection can be solved by filtering out reflected light at the reading wavelength.

Also, since the fluorescent light is incoherent, there is no problem of interference.

However, improvements remain to be made in the manufacture of such carriers. In particular, it would be desirable to decrease both the thickness and the thickness variation of the recording layers while increasing production speed and improving the information reproduction characteristics.

### Summary of the Invention

In light of the above, it is an object of the invention to decrease the thickness of the relief-carrying information layer

It is another object of the invention to decrease the layer thickness variation

It is another object of the invention to speed up the formation process for both a single layer and a multilayer structure through consecutive building-up information layers (IL).

It is another object of the invention to increase the fluorescent signal and its contrast, enabling an increase in the fluorescent carrier information capacity to reduce the requirement for a larger number of layers.

To achieve the above and other objects, the present invention is directed to a method of making a multilayer fluorescent information carrier in which a relief-carrying layer made of liquid photopolymerizing composition (PPC) is formed between a solid base disposed directly on a chuck and an overlying flexible film material, either of which should be actinic-radiation-transparent, and either of which can act as a stamper. Under the action of centrifugal forces, the relief-carrying layer is photo-solidified by light of a spectral range requisite for photopolymerization and separated from the stamper. The relief-carrying layer is then filled with a liquid composition with a fluorescent dye. The composition is photo-solidified. Single-layer film fluorescent information carriers thus formed are arranged in a

multilayer block via adhesive, cementing layers to obtain a multilayer fluorescent information carrier.

### **Brief Description of the Drawings**

Various preferred embodiments of the present invention will be set forth in detail with reference to the drawings, in which:

Fig. 1 shows a solid base placed on a centrifuge chuck;

Fig. 2 shows the application of liquid photopolymeric composition to the base to form a layer;

Fig. 3 shows irradiation of the layer with photopolymerizing light;

Fig. 4 shows the removal of the resulting replica;

Fig. 5 shows formation of an information layer from the replica;

Fig. 6 shows formation of a multilayer medium from multiple information layers; and

Fig. 7 shows an alternative technique for formation of an information layer from the replica.

### **Detailed Description of the Preferred Embodiments**

The manufacturing process for the relief-carrying layer will be described with reference to Figs. 1-6, with an alternative technique disclosed with reference to Fig. 7. Then, specific examples will be given.

The procedure takes place in a centrifuge having a centrifuge chuck 1. As shown in Fig. 1, a solid base 2 is placed on the centrifuge chuck 1. Optically transparent glass or polymer, including multilayer, substrates with pre-fabricated ILs, and nontransparent, including metal, glass or polymer substrates, can be used as a solid base. The solid base 2 has surface details (a relief pattern) 2a as required to form the relief-carrying layer.

As shown in Fig. 2, a liquid photopolymeric composition (PPC) 3 is put onto the solid base 2. Then, as shown in Fig. 3, a flexible film material 4 is applied. Either the solid base 2

or the flexible film material 4 can serve as a stamper; that is, either the solid base or the flexible material can have the required surface relief 2a. The centrifuge chuck 1 is rotated to cause the PPC to form a thin, uniform layer 3a through centrifugal force. Through varying speed, rotation time, viscosity and PPC wettability, conditions are selected for fabricating a thin, uniform PPC layer 3a between the solid base 2 and flexible material 4.

After the layer 3a with specified thickness has been formed, it is irradiated by light 5 with a spectral range appropriate for photopolymerization, thereby photopolymerizing the layer 3a to form a photopolymerized layer 3b. Then, as shown in Fig. 4, the solid base 2 and the photopolymerized layer 3b are separated, thereby forming a replica 6 having an information relief 6a.

As shown in Fig. 5, the information relief 6a is filled with a photopolymeric composition 7 with a dye (dye-in-polymer), similarly to the procedure described in the above-cited U.S. Patent No. 6,039,898, to which reference can be made for the details of that procedure. Thus, using for instance a metal matrix and a flexible transparent film, one can obtain a film carrier of a fluorescent IL, for example a film disc 8. As shown in Fig. 6, multiple film discs 8 are further arranged by means of adhesive layers 9 into a multilayer block 10, for instance, an FMD (fluorescent multilayer disc). The adhesive layer thickness is determined by external pressure and can be preset by the magnitude of that pressure. The adhesion can be achieved for instance by piling and pressing a few film discs 8 followed by photo- or thermosolidification. In the case when a flexible transparent matrix and a substrate with pre-arranged layers are used, the FMD is formed by consecutive building-up of layers similarly to the procedure proposed in the above-cited WO 99/47327 A1, to which reference can be made for the details of that procedure.

Alternatively, a relief-carrying layer can be built up by its consecutive moulding from intermediate layers of one or different PPC's on a solid base fixed on the centrifuge chuck.

To this end, one of the layer-forming substrates, for example a flexible polymer film, should easily separate from it after the solidification of the layer without affecting the surface in contact. On the surface made free from the film, again a dosed amount of PPC is applied, then covered by a flexible polymer film, centrifuged and photosolidified. Varying the PPC composition for different layers allows a wide-range change of the physical and mechanical properties of layers.

Further, the present invention provides the possibility of combining single and/or multilayer film carriers of fluorescent IL's via adhesive photosolidified layers using a centrifuge. To this end, onto the surface of one layer a dosed amount of adhesive composition is applied and covered by another layer of IL film carrier followed by leveling off in compliance with the procedure described above to obtain a replica under the action of centrifugal force. Then the adhesive layer is photosolidified. The procedure is repeated the requisite number of times to obtain a fluorescent multilayer carrier with a required number of layers.

In addition to the above-mentioned technique for filling the replica's information relief by a dye-containing polymer composition, a further duplication technique is proposed, as will be explained with reference to Fig. 7. The information relief 11a of a replica 11 formed as described above, for example, is filled by means of, for instance, spin-coating with a polymer 12, for instance photosolidified composition containing no dye. In so doing, the material for the replica and photopolymer composition is chosen such that diffusion, for instance thermodiffusion, into the material of the replica 11 is significantly slower than diffusion into the material of the polymer composition 12 filling in the information relief 11a. Thereafter, there occurs diffusion of the fluorescent dye into the polymer composition, for instance in the following way: on top of the polymer composition 12 filling the information relief 11a, a layer 13 of a fluorescent dye with or without a polymer is applied, for instance

by spin-coating. Then conditions are prescribed, for instance heating, for which the dye diffuses in the bottom polymer layer. As a result, a replica with an IL filled with a dye-in-polymer is generated. Subsequent procedures of assembling a multilayer disc are done as described above.

5 Two examples of the technique of Fig. 7 will be disclosed.

### Example 1

The layer designated to be diffused with a fluorescent dye is formed on the surface of the replica information relief from a 3 wt.% of polyacrylic acid solution in a mixture of 80% ethyl glycol, 20% isopropanol by spin-coating. On top, from the ethanol solution a layer of  
10 fluorescent dye is applied, for instance Oxazine 1, with concentration  $0.03 \text{ mol/l} \cdot 10^{-3}$ . Thereafter the replica with the applied layers is placed into a heating cabinet to be heated for 10 minutes at  $70^{\circ}\text{C}$ .

### Example 2

In a similar way to Example 1, except that the dye-free PPC from Example 8 is used  
15 as a polymer composition.

Thin-layer fluorescent polymer coats with distributed fixed luminescence centers can be prepared by using photosolidified liquid polymer compositions containing luminophores. For this purpose, onto a film formed on a centrifuge, a composition is spin-coated forming a thin liquid film distributed across the replica surface in conformity with the shape of its relief  
20 and consisting predominantly of photosolidified, generally by cation and/or radical mechanisms, monomers and oligomers and dopants determining spectral and luminescent, physical and mathematical, adhesive and other characteristics of the polymer coat following its solidification by UV light. The liquid composition applied should possess a good spreadability on the replica surface, high adhesion, and ease of forming a liquid and solidified  
25 film uniformly spread on the surface and differentially in terms of the replica relief, which

can be attained through using a specific composition as well as coating and solidification conditions. Photosolidification of the composition results in a bilayer structure with a polymer replica and a thin-film fluorescent polymer coat; said bilayer structure represents as a unit a single-layer fluorescent information carrier. From similarly generated single-layer carriers, there can be fabricated multilayer fluorescent information carriers of various types by cementing them together.

A liquid composition for a thin-film polymer fluorescent information layer (IL) comprises

- A polymerizable substance (PS) consisting of one or more substances,
- A polymerization photoinitiator consisting of one or more substances,
- A fluorescent dye (FD) consisting of one or more substances, including dyes with functional groups reactive with respect to PS, and
- An organic solvent consisting of one or more substances, including ones with functional groups reactive with respect to PS.

In addition, ILs can comprise

- a sensitizer of the polymerization photoinitiator consisting of one or more substances,
- modifiers improving film-forming and adhesive properties of the polymer layer formed, including ones containing functional groups reactive with respect to PS,
- components improving the adhesion between the surfaces of the formed IL and the adhesive or buffer layers, including at the expense of chemical reaction between them.

A PS includes photopolymerizable, predominantly by cation and/or radical mechanisms, low- and/or high-molecular components, preferably liquid. PC components can comprise functional groups photopolymerizable by both cation and radical mechanisms, with groups of different chemical nature being incorporated in both different substances and the same one simultaneously and accordingly polymerized by hybrid mechanism. For cation-



mechanism-polymerizable components there can be used cyclic esters, formals, acetals, lactones, mono- and polyfunctional epoxides, epoxyoligomers, thiiranes, vinyl monomers including fluorinated and organosilicon compounds, with epoxy compounds being most preferable. For radical-mechanism-polymerizable components there can be used substances  
 5 containing unsaturated double bonds, predominantly of (metha)acrylic type including fluorinated ones. For components polymerizable by hybrid mechanism, it is preferable to use glycidyl ethers with unsaturated double bonds. PS may comprise mono- or polyfunctional comonomers improving the PS sensitivity to the action of actinic radiation and/or physical and mechanical and/or optical and/or spectral and luminescent properties and/or adhesive  
 10 characteristics of the photosolidified information layer.

For polymerization photoinitiators, there can be used heteroorganic or metalloorganic compounds or mixtures thereof, forming homogeneous solutions with the other IL components and generating acids, predominantly Brenstead's acids and/or free radicals under the action of actinic radiation in the range 300-650 nm.

15 For fluorescent dyes, there can be used photostable dyes having a high luminescence quantum yield, forming homogeneous solutions with the other IL components, and maintaining their spectral and luminescent characteristics under IL photosolidification conditions. Dyes should be preferably chosen from the series of laser dyes.

For photopolymerization sensitizers, depending on the chemical structure of the  
 20 photoinitiator applied, there can be used individually or in mixture aromatic and heteroaromatic compounds, arylated amines, aromatic and heteroaromatic ketones and dyes with their spectra having no overlap with the absorption spectra of the fluorescent dye incorporated in the IL structure.

The fluorescent polymer layer is generated on the replica surface by spin coating of  
 25 the liquid IL composition with the components as given above, and is photosolidified by UV

radiation of specific spectral range until a solid polymer film is formed. The resulting highly-adhesive to the replica, solid-polymer, optically transparent, homogeneous, differentiated with respect to volume fluorescent layer is generated for which the topology and accordingly spatial distribution of the excited luminescence intensity are prescribed by the replica surface

5 shape and conditions of applying the liquid composition.

### Example 3

The polymerizable substance (PS) composition is prepared by mixing components as follows: Bis(4-glycidyloxyphenyl) methane (80 wt%), 1,2,7,8-Diepoxyoctane (10 wt%) and Neopentylglycol (10 wt%). To the PS, fluorescent dye (FD) Rhodamine 6G is added  
10 proceeding from  $0.01 \cdot 10^{-3} \text{M/l}$  PS. Then, a solvent is prepared consisting of 2-Ethoxyethanol, 2-Propanol and Ethanol in proportion 2:2:1 (by volume). The solvent is added to the PS-FD composition to yield a 6-wt% solution. The solution is stirred for 2 hours at  $40^\circ\text{C}$  till complete dissolving of all components of the composition mixture. Upon cooling the solution down to  $20^\circ\text{C}$ , Diphenyliodonium hexafluoroarsenate (4 wt%) is added. The resulting  
15 solution is stirred for 1 hour, filtered and used for coating the PPC replica.

### Example 4

By mixing components a PS is prepared consisting of Bisphenol A diglycidyl ether (75 wt%), 1,4-cyclohexanedimethanol diglycidyl ether (5 wt%), and 1,2,7,8-Diepoxyoctane (20 wt%). To the PS, FD Coumarin 314 is added proceeding from  $0.05 \cdot 10^{-3} \text{M/l}$  PS. Then, a  
20 solvent is prepared consisting of 2-Ethoxyethanol, 4-Hydroxy-4-methyl-2-pentanone, 2-Propanol and Ethanol in proportion 1:1:2:1 (by volume). The PS-FD composition is dissolved in the solvent  $35^\circ\text{C}$  for 4 hours to yield a 4-wt% homogeneous solution. To this solution Diphenyliodonium hexafluoroarsenate (5 wt%) is added. The resulting solution is stirred, filtered and used for coating the PPC replica.

### Example 5

By mixing components a PS is prepared consisting of Bisphenol A diglycidyl ether (70 wt%), 1,4-Butanediol diglycidyl ether (15 wt%), Bis(3,4-epoxycyclohexylmethyl) adipate (5 wt%) and neopentyl glycol ethohylate (10 wt%). To the PS, FD Coumarin 153 is added proceeding from  $0.05 \cdot 10^{-3} \text{M/l}$  PS. Then, a solvent is prepared consisting of 4-Hydroxy-4-methyl-2-pentanone, 1-Butanol, 2-Propanol, Ethyleneglycol and 2,2,3,3-Tetrafluoro-1-propanol in proportion 1:1:2:1:0.5 (by volume). The PS-FD composition is dissolved in the solvent  $40^{\circ}\text{C}$  for 3 hours to yield a 5-wt% homogeneous solution. To this solution Diphenyliodonium hexafluoroantimonate (3 wt%) is added. The resulting solution is stirred, filtered and used for coating the PPC replica.

### Example 6

By mixing components a PS composition is prepared consisting of Diglycidyl-1,2-cyclohexanedicarboxylate (45 wt%), 3-[Bis(glycidylloxymethyl)methoxy]-1,2-propanediol (45 wt%), Poly(Bisphenol A-co-epichlorohydrin),glycidyl end-capped ( $M_n = 480$ ) (2 wt%) and Dipentaerythritol (8 wt%). To the PS, FD Rhodamine 6G is added proceeding from  $0.05 \cdot 10^{-3} \text{M/l}$  PS. Then, a solvent is prepared consisting of 4-Hydroxy-4-methyl-2-pentanone, 1-Butanol, methylethyl ketone and Ethanol in proportion 2:2:1:1 (by volume). The PS-FD composition is dissolved in the solvent at  $40^{\circ}\text{C}$  for 4 hours to yield a 5-wt% homogeneous solution. To this solution then Diphenyliodonium hexafluoroarsenate and Triphenylsulfonium hexafluoroantimonate are added in proportion 1:1 to make the total catalyst concentration 3 wt% with respect to PS. Thereafter sensitizer thioxanthone is added proceeding from 10 wt% with respect to the catalyst. The solution is then stirred till complete dissolving of all components, filtered and used for coating the PPC replica.

### Example 7

By mixing components a PS composition is prepared consisting of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (80 wt%), 3-diglycidyl-1,2-cyclohexanedicarboxylate (8 wt%), Poly[(o-cresyl glycidyl ether)-co-formaldehyde] ( $M_n=$  870) (2 wt%) and Poly(caprolactone) triol ( $M_n= 300$ ) (10 wt%). To the PS, FD Oxazine 1 is added proceeding from  $0.04 \cdot 10^{-3} \text{M/l}$  PS. Then, a solvent is prepared consisting of 4-Hydroxy-4-methyl-2-pentanone, 2-Methyl-3heptanone, 3-Methyl-2-butanone and Cyclohexanone in proportion 1:1:2:2 (by volume). The PS-FD composition is then dissolved in the solvent to yield a 6-% homogeneous solution. Thereafter a solution of Triphenylsulfonium hexafluoroantimonate (20 wt%) in Propylene carbonate is prepared and added to the PS-FD solution to make the total catalyst concentration 1.5 wt% with respect to the PS. The resulting solution is then stirred, filtered and used for coating the PPC replica.

### Example 8

By mixing components a PS composition is prepared consisting of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (80 wt%), Glycerol proxylate triglycidyl ether (0.1 wt%) and Poly(vinylbutyral-co-vinylalcohol-co-vinyl acetate (9.9%). To the PS then FD Oxazine 1 is added proceeding from  $0.1 \cdot 10^{-3} \text{M/l}$  PS. Thereupon, a solvent is prepared consisting of 2-Ethoxyethanol, 1-Butanol, 2-Propanol and 3-Methyl-2-butanone in proportion 4:4:2:1 (by volume). The PS-FD composition is then dissolved in the solvent to yield a 10-% homogeneous solution. Thereafter Diphenyliodonium hexafluoroarsenate and Triphenylsulfonium hexafluoroantimonate are added to the solution in proportion 1:1 to make the total catalyst concentration 3 wt% with respect to the PS and benzophenone as 5 wt% from the catalyst. The resulting solution is then stirred, filtered and used for coating the PPC replica.

### Example 9

By mixing components a PS composition is prepared consisting of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (90 wt%), Poly(caprolactone) triol ( $M_n = 300$ ) (2 wt%) and Poly(vinylbutyral-co-vinylalcohol-co-vinyl acetate) (8%). To the  
5 PS then FD Oxazine 1 is added proceeding from  $0.06 \cdot 10^{-3} \text{ M/l}$  PS. Thereupon, a solvent is prepared consisting of 2-Ethoxyethanol, 1-Butanol, 2-Propanol and 2,2,3,3,4,4,5,5-Octafluoro-1-pentanol in proportion 1:1:1:4 (by volume). The PS-FD composition is then dissolved in the solvent to yield a 4-% homogeneous solution. Thereafter a mixture of Triphenylsulfonium hexafluoroarsenate and Triphenylsulfonium hexafluoroantimonate is  
10 added to the solution in proportion 2:1 to make the total catalyst concentration 2 wt% with respect to the PS weight. The resulting solution is then stirred till complete dissolving of all components, filtered and used for coating the PPC replica.

### Example 10

By mixing components a PS composition is prepared consisting of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (90 wt%), Glycidyl methacrylate  
15 (2 wt%) and Poly(vinylbutyral-co-vinylalcohol-co-vinyl acetate) (8%). To the PS then an FD is added consisting of a mixture of Oxazine 170 and Oxazine 1 in proportion 1:10 (by weight) proceeding from  $0.1 \cdot 10^{-3} \text{ M/l}$  PS. Thereupon, a solvent is prepared consisting of 2-Ethoxyethanol, 1-Butanol, 2-Propanol and 1,1,1,3,3,4,4,4-Octafluoro-2-butanol in proportion  
20 1:1:1:2 (by volume). The PS-FD composition is then dissolved in the solvent to yield a 3-% homogeneous solution. Thereafter Triphenylsulfonium hexafluoroantimonate is added to the solution on the basis of 1.5 wt% of the catalyst with respect to the PS weight. The resulting solution is then stirred till complete dissolving of all components, filtered and used for coating the PPC replica.

### Example 11

By mixing components a PS composition is prepared consisting of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane-carboxylate (10 wt%), 4-Vinyl-1-cyclohexane diepoxide (70 wt%), Poly(propylene glycol) diglycidyl ether ( $M_n = 640$ ) (10 wt%), and Glycidyl methacrylate (10 wt%). To the PS then FD Rhodamine 6G is added proceeding from  $0.03 \cdot 10^{-3} \text{ M/l PS}$ . Thereupon, a solvent is prepared consisting of 4-Hydroxy-4-methyl-2-pentanone, 1-Butanol, 1,1,1,5,5,6,6,6-Octafluoro-2,4-hexanedione, and Methylethyl ketone in proportion 2:2:1:1 (by volume). The PS-FD composition is then dissolved in the solvent at  $40^\circ\text{C}$  for 2 hours to yield a 3-wt% homogeneous solution. Thereafter a mixture of Triphenylsulfonium hexafluoroarsenate and Triphenylsulfonium hexafluoroantimonate is added to the solution in proportion 2:1 to make the total catalyst concentration 2.5 wt% with respect to the PS weight. The resulting solution is then stirred till complete dissolving of all components, filtered and used for coating the PPC replica.

### Example 12

By mixing components a PS composition is prepared consisting of Ethylene glycol divinyl ether (85 wt%), Di(ethylene glycol)divinyl ether (10 wt%) and Trimethylolpropane trivinyl ether (5%). To the PS then an FD is added consisting of a mixture of Coumarin 334 and Pyrromethene 567 in proportion 1:1 (by weight) proceeding from  $0.04 \cdot 10^{-3} \text{ M/l PS}$ . Thereupon, a solvent is prepared consisting of 2-Ethoxyethanol, 2-Butanol, 2-Propanol, 1,1,1,3,3,4,4,4-Octafluoro-2-butanol, 2,2,3,3-Tetrafluoro-1-propanol in equal proportions (by volume). The PS-FD composition is then dissolved in the solvent to yield a 10-% homogeneous solution. Thereafter Triphenylsulfonium hexafluoroantimonate is added to the solution on the basis of 3.5 wt% of the catalyst with respect to the PS weight. The resulting solution is then stirred till complete dissolving of all components, filtered and used for coating the PPC replica.

### Example 13

The composition as per Example 3 is spin-coated onto a PPC replica as per Example 17 at 5000 rpm. The resulting coat is then irradiated by UV light of a 500-W high-pressure mercury lamp for 8 seconds at a distance of 30 cm. Solidification of the liquid IL yields a fluorescent information carrier.

### Materials for Replica

For replica materials, PPC's are used which under the action of light transform from the liquid state to the solid state and replicate the relief of the matrix material. Depending on the fabrication technique, the thickness of the generated matrix varies in the range from 1 to 50  $\mu\text{m}$ .

For fabricating a film carrier for an IL, as a substrate for the replica, there can be used optically uniform, transparent birefringent films of at least 40 nm/mm, as well as photosolidified films of PPC prepared as described above.

The photosolidified replica material must be resistant to solvents used for IL fabrication, and be optically uniform and transparent.

For PPC materials there can be used monomers and oligomers polymerizable by radical and hybrid (radical and cation) mechanisms.

A PPC polymerizable by a radical mechanism can be composed of mono- and polyfunctional monomers and oligomers with unsaturated bonds, preferably from the (meth)acrylic series:

- vinyl monomers and polyfunctional vinyl oligomers;
- unsaturated polyesters;
- diene oligomers.

The number of monomers and oligomers in the PPC can vary from 0 to 100 wt%.

For photoinitiators of radical polymerization there can be used photoinitiators generating radicals when illuminated in the spectral range from 300 to 600 nm.

For PPC polymerizable by hybrid mechanism there can be used all the above-listed monomers and oligomers as well as mono- and polyfunctional alicyclic epoxides, epoxy-diane resins, aliphatic epoxy resins, epoxy novolacs and laproxides. To obtain requisite properties of the replica, hybrid PPCs can be doped with copolymerizable modifiers, such as simple and complex copolymerizable modifiers: simple and complex aromatic and aliphatic oligoester mono- and polyols, di- and polyfunctional alcohols, phenolformaldehyde novolacs and polyalkyleneoxides (0-50%).

For photoinitiators (0-10%) there can be used a mixture of photoinitiators generating radicals and protons (Bernstead's acids) in the spectral range 300-600 nm.

For modifiers, the PPC polymerizable by both radical and cation mechanisms can be doped with polymer materials (0-80%) compatible with PPC components both prior and following the solidification.

For sensitizers, the PPC polymerizable by both radical and cation mechanisms can also be doped with compounds that do not overlap the spectral range of the fluorescent information carrier, i.e. 300-600 nm.

PPCs used for fabricating replicas can also contain light absorbers (0-5%) in the UV visible spectral range that do not overlap the spectral range of the fluorescent information carrier operation.

#### **Example 14**

To make a PPC for a replica, 20 wt% of 1,6-hexanediol diacrylate (HDDA) (SR-238, Cray Valley), 35 wt% of ethoxylated<sub>10</sub> bisphenol A diacrylate (SR-602, Cray Valley), 20 wt% of epoxy novolac acrylate oligomer in HDDA (CN 112B70, Cray Valley), and 2 wt% of Darocure 1173 (Ciba-Geigy) are mixed at room temperature and filtered. The dosed amount



of PPC is applied onto a nickel matrix and covered by a transparent polycarbonate substrate (Fig. ). The resulting "sandwich" is irradiated by a 500-W UV-light lamp in the range 300-400 nm for 20 seconds. The solidified replica with the substrate is separated from the nickel matrix and used for IL coating.

#### 5            **Example 15**

Similar to Example 14 except that as an PPC for the replica, the following composition is used: 63 wt% of polyester acrylate (Synocure AC-1309, Cray Valley), 37 wt% of Styrene and 2 wt% of benzoin isobutyl ether .

#### **Example 16**

10           Similar to Example 14 except that as an PPC for the replica, the following composition is used: 23 wt% of modified urethane triacrylate (CN 922, Cray Valley), 5 wt% of 2-(2-ethoxyethoxy)ethylacrylate (SR 256, Cray Valley), 15 wt% of monopropyleneglycol acrylate, 57 wt% of propoxylated<sub>3</sub> trimethylopropane triacrylate (SR 352, Cray Valley), and 2 % of Irgacure 784 (Ciba-Geigy).

#### 15           **Example 17**

Similar to Example 14 except that as an PPC for the replica, the following composition is used: 20% of oligocarbonate methacrylate (OCM-2), 80% of aliphatic urethane triacrylate with  $M_n=5000$ , and 2% of Irgacure 651 (Ciba-Geigy).

#### **Example 18**

20           Similar to Example 14 except that as an PPC for the replica, the following composition is used: 50 wt% ethoxylated bisphenol A diacrylate (SR 349, Cray Valley), 10% pentaerythritol triacrylate (SR 415, Cray Valley), 40 wt% of tripropylene glycol triacrylate (SR 306, Cray Valley) and 1wt% of Irgacure 1700 (Ciba-Geigy).

### Example 19

Similar to Example 14 except that as an PPC for the replica, the following composition is used: oligocarbonate methacrylate (OCM-2, Alvar-M, Ltd.), 1% of Irgacure 651 (Ciba-Geigy) and 1% of Irgacure 1173 (Ciba-Geigy).

### 5      Example 20

Similar to Example 14 except that as an PPC for the replica, the following composition polymerizable by hybrid mechanism is used: 10% of 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate, 2% of polypropylenglycol M.W. 400, 15 wt% of tripropyleneglycol divinyl ester, 15 wt% of trimethylolpropane triacrylate  
10 (SR 351, Cray Valley), and 58 wt% of oligocarbonate methacrylate (OCM-2, Alvar-M, Ltd.); as photoinitiators, 2% Irgacure 500 (Ciba-Geigy) and 2% triarylsulfonium hexafluorophosphate are used.

### Example 21

Similar to Example 19 except that as an PPC for the replica, the following  
15 composition is used: 20 wt% of diepoxide propyleneglycol M.W. 600 (Laproxyd 603; Macromer, Ltd.), 30 wt% of bisphenol A epoxy acrylate (CN 104, Cray Valley), 50% of propoxylated<sub>2</sub> neopentyl glycol diacrylate (SR 9003, Cray Valley), 1 wt% of Irgacure 149 (Ciba-Geigy) and 1 wt% of Irgacure 261 (Ciba-Geigy).

### Example 22

20      Similar to Example 17 except that for a photoinitiator 2 wt% of phenanthrenequinone (Aldrich) and 1 wt% of triethanolamine are used.

### Example 23

Similar to Example 17 except that for a photoinitiator 2 wt% of camphorquinone (Aldrich) and 1 wt% of triethanolamine are used.

#### **Example 24**

Similar to Example 17 except that for a photoinitiator 1 wt% of Eosin B (Aldrich), 1 wt% of Dibutylaniline and 2 wt% of Irgacure 651 (Ciba-Geigy) are used.

#### **Example 25**

5        Similar to Example 19 except that as an PPC for the replica, the following composition is used: 20 wt% of poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) M.W. 70000 (Aldrich), 50 wt% of 1,6-hexanediol diacrylate, 30 wt% of 4-vinyl-1-cyclohexane 1,2-epoxide, 1 wt% of Irgacure 500 (Ciba-Geigy), 2 wt% of UVI 6974 (Union Carbide) and 2 wt% of Triarylsulfonium hexafluoroantimonate.

#### **Example 26**

10       Similar to Example 13 except that 0.1 wt% of UV absorber – 2,4,2',4'—Tetraoxybenzophenone is doped in the composition.

For sticking individual IL film carriers together in the multilayer fluorescent carrier via adhesive layers there can be used photo- and/or thermosolidified polymer compositions.

15       The adhesive material must meet the following demands:

- it must have a good adhesion with respect to the information layer PS and the film substrate material for the replica;
- it must not destroy and/or distort the fluorescent information field disposed on the relief-carrying surface of the replica;
- 20       - it must enhance the IL contrast as compared to the contrast on the single film IL carrier.

The above requirements to the adhesive material can be satisfied through using a monomeric-oligomeric composition in combination with special dopants. Such dopants bleach the fluorescent dye disposed on the surface of the replica without contacting the dye disposed in the information pit.

For PPC components for the adhesive layer there can be used the whole list of monomers and oligomers as given above with the preparation procedures described in the above-mentioned examples.

For thermosolidified components there can be used monomer and polymer resins of different functionality, laprolates , and urethane-containing monomers and oligomers.

For bleaching dopants there can be used compounds that are oxidizers with respect to the fluorescent dye, for example free radicals resulting from the initiator decomposition under the action of heat and light, as well as catalysts: aliphatic and aromatic amines.

#### **Example 27**

Similar to Example 17 except that for an adhesive layer, the PPC is also doped with 3% photoinitiator Irgacure 1700 (Ciba-Geigy).

#### **Example 28**

Similar to Example 17 except that the PPC is additionally doped with 4% benzoyl peroxide and 0.1% dibutylaniline.

While various preferred embodiments have been set forth above, it will be readily apparent that other embodiments can be realized within the scope of the invention. For example, while specific examples of compositions have been given, any other compositions having the desired qualities can be used. Also, the present invention can be adapted to the manufacture of any optical information storage medium (disc, card, etc.). Therefore, the present invention should be construed as limited only by the appended claims.